



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 050 547 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
08.11.2000 Bulletin 2000/45

(51) Int. Cl.⁷: **C08F 232/00**, **C08L 21/00**,
C08L 57/02

(21) Application number: **00109016.6**

(22) Date of filing: **27.04.2000**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **07.05.1999 US 307536**

(71) Applicant:
THE GOODYEAR TIRE & RUBBER COMPANY
Akron, Ohio 44316-0001 (US)

(72) Inventors:
• **Krlevich, Mark Leslie, Jr.**
Copley, Ohio 44321 (US)

• **Blok, Edward John**
Wadsworth, Ohio 44281 (US)
• **Widemann, Lawson Gibson**
Hudson, Ohio 44236 (US)
• **Sandstrom, Paul Harry**
Tallmadge, Ohio 44278 (US)
• **Ruscak, Joseph Miles**
Akron, Ohio 44313 (US)

(74) Representative: **Leitz, Paul**
Goodyear Technical Center-Luxembourg
Patent-Department
L-7750 Colmar-Berg (LU)

(54) **Polymeric dimethyl-dicyclopentadiene/limonene resin**

(57) This invention relates to a novel class of polymeric resins which have a softening point ranging from 50°C to 220°C and a molecular weight ranging from 500 to 42,000. The resins comprise the polymers which result from the polymerization reaction between dimethyl dicyclopentadiene and limonene. The polymeric resins are particularly useful in improving traction of the rubber when used in tire treads.

EP 1 050 547 A1

Description

Background of the Invention

[0001] This invention relates to a polymeric resin which is the reaction product of the polymerization reaction between dimethyl-dicyclopentadiene and limonene. Use of the polymeric resins of the present invention in a rubber tire stock improves the traction and handling of the tire.

Summary of the Invention

[0002] The present invention relates to a polymeric dimethyl-dicyclopentadiene/limonene resin. The polymeric resins of the present invention have softening points ranging from 50°C to 220°C, and a molecular weight of from 500 to 42,000. The present invention also includes a blend of dimethyl-dicyclopentadiene/limonene resins and rubber stocks containing the dimethyl-dicyclopentadiene/limonene resin.

Detailed Description of the Invention

[0003] The present invention relates to a polymeric resin comprising the reaction product of the polymerization reaction between dimethyl-dicyclopentadiene and limonene and having a softening point ranging from 50°C to 220°C and a molecular weight ranging from 500 to 42,000.

[0004] In addition, the present invention relates to a resin composition comprising a blend of two or more polymeric resins wherein each resin comprises the reaction product of the polymerization reaction between dimethyl-dicyclopentadiene and limonene. Alternatively, the blend can be formed in-situ; that is, the reaction temperature may be raised during the polymerization to increase the molecular weight distribution and broaden the softening point.

[0005] In addition, there is disclosed a pneumatic tire having a tread comprised of a rubber stock comprising (1) a rubber selected from the group consisting of natural rubber, rubber derived from a diene monomer or mixtures thereof, and (2) a polymeric resin composition which is the reaction product of the polymerization reaction between dimethyl-dicyclopentadiene and limonene; said resin having a softening point ranging from 50 to 220°C and a molecular weight ranging from 500 to 42,000.

[0006] There is also disclosed a rubber stock comprising (1) a rubber selected from the group consisting of natural rubber, rubber derived from a diene monomer or mixtures thereof, and (2) a polymeric resin composition which is the reaction product of the polymerization reaction between dimethyl-dicyclopentadiene and limonene; said resin having a softening point ranging from 50 to 220°C and a molecular weight ranging from 500 to 42,000.

[0007] The terms "polymeric compound" and "polymer" when used to describe the resins of the present invention are intended to only include those molecules which contain a monomeric unit derived from dimethyl-dicyclopentadiene and limonene and where at least one of the monomeric units derived from the dimethyl-dicyclopentadiene or limonene is repeated. Therefore, the compounds formed by the reaction of a single dimethyl-dicyclopentadiene molecule and a single limonene are not polymeric as the term is used herein. The term monomeric unit means a structure that occurs in a polymeric compound and which differs from the structure of dimethyl-dicyclopentadiene or limonene due to changes resulting from molecular reorientation during the linking to the adjacent structure. These changes may include addition to a double bond or the addition or removal of a hydrogen atom from the dimethyl-dicyclopentadiene or limonene.

[0008] The weight ratio of the dimethyl-dicyclopentadiene to limonene in the polymerization reaction may vary, depending on the desired properties of the final polymeric product. For example, the weight ratio of the dimethyl-dicyclopentadiene to limonene as starting material may range from 1:10 to 10:1. The preferred weight ratio of dimethyl-dicyclopentadiene to limonene may range from 5:1 to 1:5 as starting material. The most preferred ratio ranges from 2:1 to 1:2. As to the final product, the weight ratio of polymeric units derived from the dimethyl-dicyclopentadiene to limonene may range from 8:1 to 1:8. The preferred weight ratio of dimethyl-dicyclopentadiene to limonene in the final product ranges from 1:3 to 3:1 with a range of from 2.1:1 to 1:2.1, being particularly preferred.

[0009] The polymeric resinous material for use in the present invention comprises from 5 to 95 weight percent of units derived from dimethyl-dicyclopentadiene and from 95 to 5 weight percent of units derived from limonene. Preferably, the resin comprises from 33 to 67 weight percent of units derived from dimethyl-dicyclopentadiene and from 67 to 33 weight percent of units derived from limonene.

[0010] The polymeric resins may optionally be modified by the addition of up to 25 weight percent of units derived from hydrocarbons selected from C₉ and C₁₀ olefins and mixtures thereof. Therefore, at a minimum, no less than 75 weight percent of the units are derived from dimethyl-dicyclopentadiene and limonene. Preferably, from 5 to 10 weight percent of the units of the polymeric resin is derived from the above hydrocarbons.

[0011] The polymerization reaction between the dimethyl-dicyclopentadiene and the limonene may be a thermal (no catalyst) polymerization, or catalyzed, i.e., conducted in the presence of an acid catalyst. Examples of acid catalysts that may be used include Bronsted acid and Lewis acid-type catalysts. Such known acid catalysts include H₂SO₄, HCl, H₃PO₄; metal halides such as BF₃, BCl₃, AlCl₃, AlBr₃, SnCl₄, ZnCl₂, SbCl₃ and their etherates. The choice of a particular catalyst is

dependent upon factors including the melting or boiling points of the reactants, desired rate of reaction, solvent, and pressure and temperature limitation of the production equipment, etc. When higher yields are desired, the metal halides or their etherates may be utilized. The preferred acid catalysts are BF_3 and AlCl_3 . The most preferred catalyst is AlCl_3 .

[0012] In the catalyzed polymerization process, the amount of catalyst may range from 0.1 to 20 weight percent of catalyst based on the total weight of reactants to be polymerized. Preferably, a range of from 3 to 5 weight percent of catalyst is preferred. The optimum concentration of catalyst depends on the nature of the solvent, if any, which effects the solubility of the catalyst as well as on the stirring efficiency inside the polymerization reactor.

[0013] The polymerization reaction may be carried out neat (without solvent) at or above the melting points of the reactants, or can be carried out in the presence of a solvent. The solvent may be an aliphatic $\text{C}_6\text{-C}_{12}$ hydrocarbon, an aromatic or haloaromatic ($\text{C}_6\text{-C}_9$) hydrocarbon, or a $\text{C}_6\text{-C}_9$ aliphatic halohydrocarbon. Examples of suitable solvents include hexane, heptane, cyclohexane, benzene, toluene, xylene, and chlorobenzene. The preferred solvents are heptane and cyclohexane.

[0014] The polymerization reaction may be conducted under a variety of operating conditions. The reaction pressure may vary and range from one atmosphere to 100 atmospheres with a pressure of from two atmospheres to ten atmospheres being preferred. The reaction temperature may range from 0 to 100 °C with a preferred range being from 25 to 50°C.

[0015] Depending on the reactivity of the reactants, amount of catalyst, reaction pressure and reaction temperature, the reaction time may vary. Generally speaking, the reaction time varies from 1 to 8 hours.

[0016] The molecular weight distribution of the polymeric resin of the present invention may range from 500 to 42,000. In a particularly preferred embodiment of the present invention, the resin composition may have a molecular weight distribution of from 500 to 29,500. The resin may comprise a blend of two or more individual polymeric resins each one of which is the reaction product of a polymerization reaction between dimethyl-dicyclopentadiene and limonene. Each individual polymeric resin preferably differs from the other by having a different molecular weight range. Generally speaking, all of the polymeric resins will exhibit some lower molecular weight values, however, not all of the individual resins may include the higher molecular values. In the alternative, all of the resins may have distributions that vary by their lower molecular values with the high molecular weight value relatively being the same. For example, when the resin blend comprises three individual polymeric resins, the first resin may have a molecular weight ranging from 700 to 24,000, the second resin may have a molecular weight ranging from 700 to 36,000, and the

third resin may have a molecular weight ranging from 700 to 42,000.

[0017] In accordance to another embodiment of the present invention, the resin composition may comprise a blend of four individual resins. In accordance with this embodiment, the first resin may have a molecular weight ranging from 500 to 15,000, the second resin may have a molecular weight ranging from 700 to 15,000, the third resin may have a molecular weight ranging from 3,000 to 15,000, and the fourth resin may have a molecular weight ranging from 4,000 to 15,000.

[0018] The blend may be formed in-situ or mechanically blended.

[0019] The resin composition of the present invention has a softening point ranging from 50 to 220°C. For the purposes of the present invention, the term "softening point" is used to describe the temperature range from when wetting occurs in a capillary melting point tube to where the resin is completely liquid. Representative of suitable equipment to determine the relative softening point is a Thomas-Hoover Melting Point apparatus equipped with a silicon oil bath.

[0020] Rubber stocks containing natural rubber or rubbers derived from a diene monomer may be modified with the resin compositions of the present invention. Examples of rubbers derived from a diene monomer include substituted and unsubstituted, saturated and unsaturated, synthetic polymers. The natural polymers include natural rubber in its various forms, e.g., pale crepe and smoked sheet, and balata and gutta percha. The synthetic polymers include those prepared from a single monomer (homopolymer) or a mixture of two or more copolymerizable monomers (copolymer) when the monomers are combined in the random distribution or block form. In addition to the diene monomers, other monomers may be used. Of all the monomers that may be used, the monomers may be substituted or unsubstituted and may possess one or more double bonds, for example, diene monomers, both conjugated and non-conjugated, and monoolefins, including cyclic and acyclic monoolefins, especially vinyl and vinylidene monomers. Examples of conjugated dienes are 1,3-butadiene, isoprene, chloroprene, 2-ethyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene. Examples of nonconjugated dienes are 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 1,5-cyclooctadiene and ethylidene norbornene. Examples of acyclic monoolefins are ethylene, propylene, 1-butene, isobutylene, 1-pentene and 1-hexene. Examples of cyclic monoolefins are cyclopentene, cyclohexene, cycloheptene, cyclooctene and 4-methylcyclooctene. Examples of vinyl monomers are styrene, acrylonitrile, acrylic acid, ethylacrylate, vinyl chloride, butylacrylate, methyl vinyl ether, vinyl acetate and vinyl pyridine. Examples of vinylidene monomers are alpha-methylstyrene, methacrylic acid, methyl methacrylate, itaconic acid, ethyl methacrylate, glycidyl methacrylate and vinylidene chloride. Representative examples of the synthetic polymers used in the practice of this invention

are polychloroprene, homopolymers of a conjugated 1,3-diene such as isoprene and butadiene, and in particular, polyisoprenes and polybutadienes having essentially all of their repeat units combined in a cis-1,4-structure; and copolymers of a conjugated 1,3-diene such as isoprene and butadiene with up to 50 percent by weight of at least one copolymerizable monomer, including ethylenically unsaturated monomers such as styrene or acrylonitrile; and butyl rubber, which is a polymerization product of a major proportion of a monoolefin and a minor proportion of a diolefin such as butadiene or isoprene.

[0021] The rubber compounds which may be modified by the resins of the present invention are preferably cis-1,4-polyisoprene (natural or synthetic), polybutadiene, polychloroprene and the copolymers of isoprene and butadiene, copolymers of acrylonitrile and butadiene, copolymers of acrylonitrile and isoprene, copolymers of styrene, butadiene and isoprene, copolymers of styrene and butadiene, copolymers of styrene and isoprene and blends thereof.

[0022] The amount of polymeric resins that may be used with the diene containing polymers may vary and depend on the polymer to be modified, the particular polymeric resin, the desired degree of modification and the like. Generally speaking, the polymeric resin is used in amounts ranging from 5 to 50 parts per hundred (phr) of diene polymer. Preferably, the polymeric resin is used in amounts of from 5 to 25 phr, with a range of from 10 to 25 phr being particularly preferred.

[0023] The polymeric resins may be incorporated in the diene containing polymer by conventional mixing procedures, for example, by adding them in a banbury mixer or by adding them to the rubber on a mill. Preferably, when the polymeric resins have higher molecular weights, it is recommended that they be ground to a fine powder to insure adequate dispersion. Such powders may be treated to suppress dust, for example, by the addition of oil, or they can be mixed with a binder, for example, a polymer latex, and granules or pellets containing up to 5 percent by weight of a binder. They can also be formulated as pre-dispersions or masterbatched in a diene rubber stock, which pre-dispersions may contain, for example, from 15 to 50 percent by weight of the polymeric resin.

[0024] Similar to vulcanizing conventional rubber stocks, the rubber stocks containing the polymeric resins need a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. The amount of sulfur vulcanizing agent will vary depending on the components of the rubber stock and the particular type of sulfur vulcanizing agent that is used. Generally speaking, the amount of sulfur vulcanizing agent ranges from 0.1 to 8 phr with a range of from 1.5 to 6 being preferred.

[0025] Conventional rubber additives may be incorporated in the rubber stock of the present invention. The presence of a sulfur vulcanizing agent and conventional additives are not considered to be an aspect of this invention. The additives commonly used in rubber stocks include fillers, plasticizers, curatives, processing oils, retarders, antiozonants, antioxidants and the like. The total amount of filler that may be used may range from 45 to 130 phr being preferred. Fillers include silicas, clays, calcium carbonate, calcium silicate, titanium dioxide and carbon black. Preferably, at least a portion of the filler is carbon black. Plasticizers, oils or mixtures thereof are conventionally used in amounts ranging from 2 to 90 phr with a range of 5 to 70 phr being preferred. The amount of plasticizer used will depend upon the softening effect desired. Examples of suitable plasticizers include aromatic extract oils, petroleum softeners including asphaltenes, saturated and unsaturated hydrocarbons and nitrogen bases, coal tar products, cumarone-indene resins and esters such as dibutylphthalate and tricresyl phosphate. Examples of oils are commonly known as highly aromatic process oil, process soybean oil and highly paraffinic process oil. Materials used in compounding which function as an accelerator-activator includes metal oxides such as zinc oxide, magnesium oxide and litharge which are used in conjunction with acidic materials such as fatty acid, for example, stearic acid, oleic acid, murastic acid, and the like. The amount of the metal oxide may range from 1 to 10 phr with a range of from 2 to 8 phr being preferred. The amount of fatty acid which may be used may range from 0.25 phr to 5.0 phr with a range of from 0.5 phr to 2 phr being preferred.

[0026] Accelerators may be used to control the time and/or temperature required for vulcanization of the rubber stock. As known to those skilled in the art, a single accelerator may be used which is present in amounts ranging from 0.2 to 3.0 phr. In the alternative, combinations of two or more accelerators may be used which consist of a primary accelerator which is generally used in a larger amount (0.3 to 3.0 phr), and a secondary accelerator which is generally used in smaller amounts (0.05 to 1.50 phr) in order to activate and improve the properties of the rubber stock. Combinations of these accelerators have been known to produce synergistic effects on the final properties and are somewhat better than those produced by use of either accelerator alone. Delayed action accelerators also are known to be used which are not affected by normal processing temperatures and produce satisfactory cures at ordinary vulcanization temperatures. Suitable types of accelerators include amines, disulfides, guanidines, thioureas, thiazoles, thurams, sulfenamides, dithiocarbamates and the xanthates. Examples of specific compounds which are suitable include zinc diethyl-dithiocarbamate, 4,4'-dithiodimorpholine, N,N-di-methyl-S-tert-butylsulfenyldithiocarbamate, tetramethylthiuram disulfide, 2,2'-dibenzothiazyl disulfide, butyraldehydeaniline mercap-

tobenzothiazole, N-oxydiethylene-2-benzothiazolesulfenamide. Preferably, the accelerator is a sulfenamide.

[0027] A class of compounding materials known as scorch retarders are commonly used. Phthalic anhydride, salicylic acid, sodium acetate and N-cyclohexyl thiophthalimide are known retarders. Retarders are generally used in an amount ranging from 0.1 to 0.5 phr.

[0028] Preformed phenol-formaldehyde type resins may be used in the rubber stock and are generally present in an amount ranging from 1.0 to 5.0 phr, with a range of from 1.5 to 3.5 phr being preferred.

[0029] Conventionally, antioxidants and some times antiozonants, hereinafter referred to as antidegradants, are added to rubber stocks. Representative antidegradants include monophenols, bisphenols, thiobisphenols, polyphenols, hydroquinone derivatives, phosphites, thioesters, naphthyl amines, diphenyl-p-phenylenediamines, diphenylamines and other diaryl amine derivatives, para-phenylenediamines, quinolines and mixtures thereof. Specific examples of such antidegradants are disclosed in The Vanderbilt Rubber Handbook (1990), pages 282-286. Antidegradants are generally used in amounts from 0.25 to 5.0 phr with a range of from 1.0 to 3.0 phr being preferred.

[0030] The mixing of the rubber composition can be accomplished by methods known to those having skill in the rubber mixing art. For example, the ingredients are typically mixed in at least two stages; namely, at least one non-productive stage followed by a productive mix stage. The final curatives including sulfur vulcanizing agents are typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The rubber and polymeric resin are mixed in one or more non-productive mix stages. The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art.

[0031] Vulcanization of the pneumatic tire of the present invention is generally carried out at conventional temperatures ranging from 100°C to 200°C. Preferably, the vulcanization is conducted at temperatures ranging from 110°C to 180°C. Any of the usual vulcanization processes may be used such as heating in a press or mold, heating with superheated steam or hot air or in a salt bath.

[0032] The following examples are presented in order to illustrate but not limit the present invention.

[0033] In the following examples, the Flexsys Rubber Process Analyzer (RPA) 2000 was used to determine dynamic mechanical rheological properties. The curing conditions were 160°C, 1.667 Hz, 15.8 minutes and 0.7 percent strain. A description of the RPA 2000, its capability, sample preparation, tests and subtests can be found in these references. H A Pawlowski and J S Dick, Rubber World, June 1992; J S Dick and H A

Pawlowski, Rubber World, January 1997; and J S Dick and J A Pawlowski, Rubber & Plastics News, April 26 and May 10, 1993.

[0034] The compounded rubber sample is placed on the bottom die. When the dies are brought together, the sample is in a pressurized cavity where it will be subjected to a sinusoidal oscillating shearing action of the bottom die. A torque transducer connected to the upper die measures the amount of torque transmitted through the sample as a result of the oscillations. Torque is translated into the shear modulus, G, by correcting for the die form factor and the strain. The RPA 2000 is capable of testing uncured or cured rubber with a high degree of repeatability and reproducibility. The tests and subtests available include frequency sweeps at constant temperature and strain, curing at constant temperature and frequency, strain sweeps at constant temperature and frequency and temperature sweeps at constant strain and frequency. The accuracy and precision of the instrument allows reproducible detection of changes in the compounded sample.

[0035] The values reported for the storage modulus, (G'), loss compliance (J'') and tan delta are obtained from a strain sweep at 100°C and 1 Hz following the cure test. These properties represent the viscoelastic response of a test sample to shear deformation at a constant temperature and frequency.

[0036] The following examples are presented for the purposes of illustrating and not limiting the present invention. All parts are parts by weight unless specifically identified otherwise.

Example 1

[0037] A three liter round bottom flask was fitted with a mechanical stirrer, a constant temperature water bath, a thermocouple and a dropping funnel. The flask was swept with nitrogen and charged with 200 milliliters of cyclohexane containing 50 grams of anhydrous aluminum chloride. Stirring was started and the water bath raised the temperature of the aluminum chloride/cyclohexane suspension to 30°C. The dropping funnel was charged with a solution of 200 ml of cyclohexane, 200 grams of dimethyl-dicyclopentadiene and 200 grams of (+)-limonene of technical grade from Eastman Kodak. The feed stream was added as quickly as possible with the reaction temperature maintained at 25-30°C. After 35-40 minutes, all of the feed had been added and the reaction temperature of 25-30°C was maintained for a total residence time of two hours with stirring. A solution of 4 liters of isopropanol and 2 liters of water was treated with the reaction mixture. The aqueous-organic mixture was stirred vigorously until all of the catalyst had been hydrolyzed. The organic layer which contains a suspended solid was separated and washed with two portions of 2 liters of water. The organic layer which contained the suspended solid was dried in a drying oven at 70°C and 29 inches of mercury

vacuum. The product softens or shows wetting in a capillary melting point tube at 142-163°C. Small molecule GPC analysis gives a molecular weight distribution of 6.5 percent in the 29,500 MW range, 22.9 percent in the 15,600 MW range and 41.8 percent in the 4100 MW range and 26.2 percent in the 1610 MW range and 2.6 percent in the 430 MW range.

Example 2

[0038] In this example, the resin prepared in accordance with Example 1 was evaluated in a rubber compound.

[0039] Rubber compositions containing the materials set out in Table I were prepared in a BR Banbury™ mixer using two separate stages of addition (mixing); namely, one non-productive mix stage and one productive mix stage. The non-productive stage was mixed for 3.5 minutes or to a rubber temperature of 160°C, whichever occurred first. The mixing time for the productive stage was to a rubber temperature of 120°C.

[0040] The rubber compositions are identified herein as Samples 1 and 2. Sample 1 is considered herein as a control without the use of the resin used in the present invention being added to the rubber composition. Sample 1 contains a commercially available aromatic resin. Sample 2 contains the resin prepared in Example 1.

[0041] The samples were cured at 150°C for 28 minutes.

[0042] Table II illustrates the behavior and physical properties of the cured Samples 1 and 2.

[0043] The Dimethyl DCPD/Limonene resin of Example 1 in Sample 2 imparts a durability advantage with equal dry traction over the Coumarone Indene control (Sample 1). More cornering stiffness and better handling is provided due to the significant increase in 300 percent modulus and dynamic modulus (G') at 40 percent strain. Room Temperature Tensile Strength, 100C Tensile Strength and Energy to Break at 100C are maintained or increased which will improve the graining and blistering resistance of the tread. The loss compliance (J'') and tan delta at 40 percent strain were maintained or improved which indicates equal or improved traction. This resin improves the tradeoff between traction and durability that is present with conventional materials.

Table I

Samples	Ctrl 1	2
Non-Productive		
Solution SBR ¹	100	100
Carbon Black ²	90.0	90.0
Aromatic Oil	45	45
Stearic Acid	1.0	1.0
Zinc Oxide	1.25	3.0
Antioxidant ³	0.7	0.7
Coumarone Indene ⁴ Resin	20	0
Resin of Example 1	0	20
Productive		
Accelerators ⁵	2.5	2.5
Accelerator ⁶	0.21	0.21
Sulfur	1.28	1.28

¹Solution SBR containing 32 percent styrene, a vinyl content of 42 percent, a Tg of -16°C and a base Mooney of 85-95. The solution SBR was obtained from The Goodyear Tire & Rubber Company.

²I₂=122 and DBP=114

³Polymerized 1,2-dihydro-2,2,4-trimethylquinoline

⁴Coumarone Indene Resin having a softening point of 100°C which is commercially available from Neville Chemical under the designation Cumar™ R-13.

⁵N-cyclohexyl benzothiazole-2-sulfenamide

⁶Tetramethyl thiuram disulfide

Table II

Samples	1	2
Coumarone Indene Resin	20	0
Resin of Ex 1	0	20
UTS, cured @ 28/150		
Modulus, 300% (MPa)	4.8	6
Break Str (MPa)	11.4	11.4
Elongation, %	610	568
HOT (100C) UTS, cured @ 28 min @ 150°C		
Modulus, 300% (MPa)	3.26	3.85
Break Str (MPa)	7.2	7.85
Elongation, %	584	583
Energy (N-cm)	610	729
RPA 2000 Cure: 160°C, 1.677 Hz, 15.8 min, 0.7% Strain		
Min Torque	0.66	0.75
Max Torque	3.35	4.07
Delta Torque	2.69	3.32
T'02 (min)	0.52	0.178
T'25 (min)	2.17	1.69
T'90 (min)	8.43	8.27
Strain Sweep: 1000, 11 Hz		
G' (kPa) at 40% Strain	526	600
Tan Delta at 40% Strain	0.252	0.297
J" (1/MPa) at 40% Strain	0.451	0.455

Claims

1. A resin composition characterized by being a polymer which is the reaction product of the polymerization reaction between dimethyl-dicyclopentadiene and limonene, said resin having a softening point ranging from 50 to 220°C and a molecular weight ranging from 500 to 42,000.
2. The resin composition of claim 1 further characterized by a blend of two or more resins, wherein each resin is the reaction product of the polymerization reaction between dimethyl-dicyclopentadiene and limonene and each resin has a softening point ranging from 50 to 220°C and a molecular weight ranging from 500 to 42,000.
3. The resin composition of claim 1 characterized in that said composition is the polymerization reaction product of from 10 to 1 parts by weight of dimethyl-dicyclopentadiene and from 1 to 10 parts by weight of limonene.
4. The resin composition of claim 1 characterized in that from 5 to 95 weight percent of units derived from dimethyl-dicyclopentadiene and from 95 to 5 weight percent of units derived from limonene.
5. The resin composition of claim 1 further characterized by containing up to 25 weight percent of units derived from hydrocarbons selected from the group consisting of C₉ and C₁₀ olefins.
6. A rubber stock characterized by (1) a rubber selected from the group consisting of natural rubber, rubbers derived from a diene monomer or mixtures thereof, and (2) a polymeric resin of any of claims 1 through 5.
7. The rubber stock of claim 6 wherein said rubber derived from a diene monomer or mixtures thereof is selected from the group comprising natural rubber, polyisoprene, polybutadiene, polychloroprene, copolymers of isoprene and butadiene, copolymers of acrylonitrile and butadiene, copolymers of acrylonitrile and isoprene, copolymers of styrene, butadiene and isoprene, copolymers of styrene and butadiene, copolymers of styrene and isoprene and blends thereof.
8. The rubber stock of claim 6 characterized in that said polymeric resin composition is present in an amount ranging from 5 to 50 parts per hundred parts of rubber.
9. A pneumatic tire having a tread characterized by the rubber stock of any of claims 6 through 8.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 10 9016

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 5 691 432 A (WILLIAMS THEODORE JOSEPH) 25 November 1997 (1997-11-25) * column 8, line 7 - line 13 * * claim 1 *	1-9	C08F232/00 C08L21/00 C08L57/02
A	US 4 157 363 A (HEPWORTH PAUL) 5 June 1979 (1979-06-05) * examples * * claim 1 *	1-9	
A	US 4 968 764 A (HAYASHIDA SUETOU ET AL) 6 November 1990 (1990-11-06) * abstract * * examples *	1-9	
A	EP 0 011 393 A (EXXON RESEARCH ENGINEERING CO) 28 May 1980 (1980-05-28) * abstract *	1-9	
A	GB 1 107 329 A (MONTECATINI) 27 March 1968 (1968-03-27) * examples *	1-9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08F C08L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 July 2000	Examiner Pol110, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.92 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 10 9016

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-07-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5691432 A	25-11-1997	US 5410004 A	25-04-1995
		US 5693731 A	02-12-1997
		CA 2140565 A	25-07-1995
		DE 69508813 D	12-05-1999
		DE 69508813 T	05-08-1999
		EP 0665246 A	02-08-1995
		JP 8048723 A	20-02-1996
US 4157363 A	05-06-1979	GB 1548568 A	18-07-1979
		AU 1662776 A	09-02-1978
		DE 2636936 A	03-03-1977
		DK 372276 A	21-02-1977
		ES 450865 A	01-09-1977
		FI 762385 A,B,	21-02-1977
		FR 2321517 A	18-03-1977
		IT 1074417 B	20-04-1985
		JP 52027449 A	01-03-1977
		JP 59033137 B	14-08-1984
		NL 7609158 A	22-02-1977
		BE 845199 A	14-02-1977
US 4968764 A	06-11-1990	JP 2517233 B	24-07-1996
		JP 62295933 A	23-12-1987
		DE 3781465 A	08-10-1992
		DE 3781465 T	18-03-1993
		EP 0249904 A	23-12-1987
		KR 9604355 B	02-04-1996
EP 0011393 A	28-05-1980	GB 2032442 A	08-05-1980
		CA 1185399 A	09-04-1985
		DE 2964374 D	27-01-1983
		DK 443179 A,B,	21-04-1980
		JP 1476226 C	18-01-1989
		JP 55056113 A	24-04-1980
		JP 63027367 B	02-06-1988
		JP 63099207 A	30-04-1988
GB 1107329 A		DE 1620601 A	26-02-1970
		FR 1447845 A	07-11-1966
		NL 6510532 A	29-03-1966

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office. No. 12/82